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Phase-Transfer Catalyzed Generation of Dimethylvinylidene Carbene [1]

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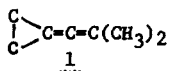
Reaction of a 1-halo-3-methyl-1,2-butadiene or a 3-halo-3-methyl-1-butyne with potassium tert-butoxide in the presence of an olefin is commonly used for the preparation of dimethylvinylidenecyclopropanes (1) through trapping of dimethylvinylidene carbene (2). Strictly controlled anhydrous conditions are required and product yields are only moderate.[2,3]

As shown here, 2 may be conveniently prepared from 1 generated from the reaction of 1-bromo-3-methyl-1,2-butadiene[4] (3 g) with hydroxide ion in a two-phase olefin (20 ml)-50% sodium hydroxide (7 ml) system containing tricapyrylmethylammonium chloride[5] (1 g) as a phase-transfer catalyst[5] (0-60°). Yields of dimethylvinylidenecyclopropanes are 20-40% higher using the phase-transfer catalysis instead of t-BuOH-free potassium tert-butoxide, and 23-69% higher than potassium tert-butoxide tert-butylacohol-induced reactions. Yields are summarized in Table 1. The phase-transfer catalyzed reactions exhibited time dependence for maximum yield whereas potassium tert-butoxide-induced reactions exhibited maximum yield after 2 hr. (0-5°).

Table I

Yields of Dimethylvinylidenecyclopropanes (1)



1

Olefin	$(C_8H_{18})_3NCH_3Cl$[a,b]	t-BuOK[a]	t-BuOK · t-BuOH[a]	Ref. 2[c]
$(CH_3)_2C=C(CH_3)_2$	68 (16 hr)	48	22	47
$(CH_3)_2C=CHCH_3$	84 (25 hr)	46	15	36
Cyclohexene	61 (48 hr)	18	14	26
$CH_3(CH_2)_3CH=CH_2$	25 (72 hr)	4.3	1.8	12

a) Vpc yields. b) Isolated yields of pure product were 2-5% lower than the vpc yield.

c) Isolated yield of pure product.

The reactivity of 2 towards the olefins studied (Table II) exhibits much independence from both the precursor and the method of generation except for the t-BuOH free t-BuOK-induced reaction where 2 shows slightly higher reactivity. This could mean that the nature of 2 is not the same in all base-induced reactions, but more data are necessary before confident mechanistic interpretations can be made.

Table II[7]

Relative Rates of Dimethylvinylidene Carbene Addition to Olefins

$(CH_3)_2C{=}C{=}C{:}$[a]

2

Olefin	$(C_8H_{18})_3NCH_3Cl$	t-BuOK	t-BuOK • tBuOH	Ref. 8[b]
$(CH_3)_2C{=}C(CH_3)_2$	19.3	7.4	14.7	15.8
$(CH_3)_2C{=}CHCH_3$	6.6	4.3	5.5	4.9
Cyclohexene	1	1	1	1
$CH_3(CH_2)_3CH{=}CH_2$	0.2	0.3	0.2	0.2

a) 0-5°. b) Generated from 1-chloro-3-methyl-1,2-butadiene and t-BuOK at -10°.

References

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